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The Effect of Different Reducing Agents in the Distillation of Zinc

THE EFFECT OF DIFFERENT REDUCING AGENTS IN THE DISTILLATION OF ZINC

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

OTTO ALBERT PROELSS

ENTITLED THE EFFECT OF DIFFERENT REDUCING AGENTS IN THE DISTILLATION OF ZINC

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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This investigation was carried out in the Chemical Laboratory of the University of Illinois during the year 1919-1920.

It was undertaken at the suggestion of Dr. Gerlach of the Matthiessen and Hegeler Zinc Co. and carried out under the direction of Dr. McFarland.

The writer takes this opportunity to express his appreciation to Dr.Gerlach and Dr.McFarland for the helpful direction and assistance which was given throughout the work.

TABLE OF CONTENTS

THE EFFECT OF DIFFERENT REDUCING AGENTS IN THE DISTILLATION OF ZINC.

I.

INTRODUCTION

A. Object

During the year following the close of the war, the transportation system of the country showed signs of breaking down and it became exceedingly difficult to obtain shipments of fuel. This, coupled with the fuel strike, caused industries like the zinc smelting business to soon feel the strain. The standard practice is to mix the roasted ore with about 42% of anthracite culm for the reducing agent. If some mixture of locally produced fuels would give the same or better recovery as that obtained with culm, then these fuels could be substituted and leave the zinc smelter independent of the long haul connected with the use of remote anthracite. With this object in view, different reducing agents were investigated and their action on the recovery of metal and blue powder compared with the values obtained with the use of anthracite culm.

B. Previous Work

A review of the literature does not show any experiments in which the operator attempted to double his results by the use of materials or conditions which are met with in large scale practice. There have been experiments conducted in which zinc oxide was reduced with different agents, using small iron or quartz tubes for the retort. Crude petroleum was used as a reducing agent in a method using a continuous process furnace. (1) The reaction was

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(1) [illegible] and [illegible], J. Ind. Eng. Chem. I, 700.

supposed to occur when both ZnO and the reducing agent were in a gaseous condition. It did not prove to be a commercial success.

H. Koppers (2) recommended as reducing agent a fine grained coke, obtained by subjecting normal non-coking bituminous coal to partial distillation and ignition in a rotating oven.

Gas in the form of hydrogen is said by Gillet (3) to completely reduce ZnO in a hot glass tube.

Natural gas was tried in some plants in Kansas in the early days but was given up as impracticable.

The alkali earth carbides have been experimented with (4) but they were found in this investigation to require too high a temperature of decomposition for practical use.

From time to time, different smelters have tried one or more substitutions of reducing material but they have not given out any information they secured so that it has been impossible to compare the data secured in this research with that of any other similar operation.

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(2) H. Koppers, Ger. Pat. 249141 Jan. 24, 1911.

(3) C. Gillet, Bull. Soc. Chim. Belg. 26, 106-7.

(4) Reference lost.

II.

SUMMARY OF RESULTS

(1) The substitution of coke for a like percentage of culm does not give as much recovery of metal.

(2) Oil can not be substituted for culm if the amount of culm is reduced below 40%.

(3) If the amount of culm is at least 40%, then the addition of oil leads to greater recoveries.

(4) If coke is used in amounts of 40% or better, then an addition of oil will give the results obtained with 40% of culm.

(5) Oil seems to give to coke the required features for a good reducing agent.

(6) Increasing the percent of culm above 40% gave greater increased recoveries than the percent of extra reducing agent added.

(7) Adding oil to 40% culm increases the recovery about as much as would be obtained with 1/3 the amount of culm.

(8) Charcoal gives 19% more recovery than the same amount of culm.

(9) The use of 30% of lignite gives 6.5% more recovery than 40% culm but gives 25% less recovery than the same amount of culm.

(10) Pitch gives very low recoveries of metal but an excess of this agent gave a large recovery of nearly pure zinc powder.

(11) Calcium carbide was a complete failure as a reducing agent.

(12) An analysis of the retort residues shows that the two powdered fuels, (charcoal and lignite)tho giving satisfactory recoveries, left a residue containing a high percent of zinc, very little being lost thru volatilization and absorption.

III.

RECOMMENDATIONS

(A) Economy.

From the work, it was shown that to get good recoveries of zinc the reducing agent must be used in great excess to effect the reduction. The increase of culm from 40 to 50% increased the recovery 15.5%. At this rate it would pay to use a great excess of reducing agent and later wash out the coal left. In the residues charcoal gives an increase of 15% over the same percent of culm, and leaves the rest of the zinc in the residues in sufficient amount to concentrate for the zinc content. The best substituting agent seems to be coke with some addition of volatile agent as oil. It may be that more volatile coals as lignite or Eastern bit. could produce the same effect as oil. The development of a coke containing some volatile would be just as effective. If lignite in slightly greater proportions than that used with culm, is tried, recoveries as great as with 40% culm are obtained and in addition a residue containing 41.2% zinc. This residue is high enough in zinc content to be charged direct into the cooler sections of the furnace after the addition of a little more reducing agent.

(B) Financial.

Aside from the theoretical yield of zinc, there is to be considered the cost of the proposed reducing agent. The high cost of charcoal would prohibit the use of this agent at any time. With anthracite at about $15.00 per ton delivered and coke selling from $12.00 to $14.00 per ton, along with oil at $4.00 per barrel makes the use of oil and coke too costly. This might be offset by the use of lignite instead of the oil. The use of lignite alone would prove the cheapest.

(c) Further Research

Before one could use the proposed suggestions, it would be necessary to try them for a period in actual conditions, using one of the retorts in a zinc furnace for the test. Then from the recoveries and costs, the manager could decide which would give the greatest recovery at the least cost.

Other charges that should be tried are;

(1); 50% coke
(2); 40% coke and 10% lignite
(3); 40% lignite
(4); 40% bit. coal
(5); 50% bit. coal
(6); mixtures of coke and lignite
(7); " " " " bit. coal
(8); " " bit. coal and lignite
(9); gases, such as CO; producer gas; blast furnace gas and other waste gases.

II.

EXPERIMENTAL

(A.) Construction of Furnace

The furnace used in this work was built with the aid of Thomas H. McCormack and is written up in detail in his thesis entitled, "A Zinc Distillation Furnace." It was built with the idea of having it correspond to a miniature zinc furnace, i.e. to furnish the same conditions of operation. It had double walls of fire brick, floor of the same material covered with a porcelain glaze, and a roof composed of two fire brick slabs. In size it accomodated one retort inclined at about 10 degrees to a bench at the rear. The retort was first used supported only at the ends but due to excessive bending in the middle, a brick support was placed at the center. Directly under the retort running from front to rear was an inverted V shaped mound of broken fire brick to deflect the heat upwards against the retort. The heating element was city gas fed in at both sides thru three pipes placed at staggered intervals from those on the opposite side. Enclosing the gas pipe was another pipe thru which a blast of air was fed. There were valves for each of the six gas and air connections. Figure A of Plate II. shows a cross section of the furnace; figure B a plan, and figure C a front elevation.

B. Making of Retorts

A mold for the manufacture of clay retorts was loaned thru the courtesy of Dr. [illegible]. Gerlach, who had used it in making them for a similar purpose. The clay used was a standard mix and was furnished by the United Zinc Smelting Corp. of Moundsville W. Va. It was about 55% calcined grog and 45% raw St Louis fire clay.

A great deal of difficulty was experienced in trying to make the retorts with the retort mold as [illegible] Fig. III. The clay showed a tendency to stick to the inner pipe when it was withdrawn. Numerous degrees of wetness were tried and the pipe greased with oil, but even then when the mold was clamped together it was either impossible to withdraw the pipe or else the clay would come out with it. Finally it was decided to make each half separately and trust to the clamping effect to weld the joints together. This method succeeded and after the retort had stood for two days it had contracted enough to be slipped out of the mold.

A retort made in this manner was not exactly smooth inside and its walls were not of a [illegible] dimensions but these irregularities are of small consequence in the recovery of zinc compared with the well known tendency of all retorts, whether hand made or by press, to absorb zinc, to crack and form injurious cavities and pockets.

The retort after drying was about 20 in. long, [illegible] in. wide with walls of 5/8 in. and was capable of holding a charge of 500 grams of ore mixed with [illegible] grams of coal.

C. Distillation

(1) Temperature

When roasted zinc ore is mixed with an excess of reducing agent and heated to a high temperature, the metal is reduced in the form of vapor, which is subsequently liquefied by cooling, in practice a point between 415°C. and 550°C.(5) According to C. Boudouard (6) experiments show a slight development of gas

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(5) Ingalls, "Metallurgy of Zinc"

(6) C. Boudouard, [illegible]

at 800°C. which soon ceased. Regular reaction does not begin until 1125 to 1150°C. is attained. E. Prost (7) found that reduction begins with pure ZnO at 1075°C. According to R.C.Schuepphaus (8) the reduction begins at 910°C. but does not become active until higher temperatures are reached.

The maximum temperature that was ever used in the present work was 1250°C. but the general working temperature was about 1150°C. The following table shows a representative list of temperatures taken during the operation of distilling a charge.

TABLE No. 1.

2.30	P.M.	Charged	750°C	(Retort)
3.30	"		1150°C.	(Furnace)
4.00	"		1120°C.	"
4.30	"	Draw	1120°C.	"
4.45	"		1150°C.	"
5.00	"		1125°C.	"
5.30	"	Draw	1120°C.	"
"	"		1070°C.	(Retort)
"	"		470°C.	(Condenser)

It is seen that after the furnace gets heated up the temperature of the retort is only about 50°C. below that of the furnace. The thermo-chemical equations show that an enormous amount of heat is required for the operation as all the reactions are endothermic and require heat to be supplied to them.

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(7) E.Prost, Journ. Soc.Chem.Ind. 1898 p. [illegible].

(8) R.C.Schuepphaus, Journ.Soc.Chem.Ind. Vol.[illegible], 1899, p.[illegible].

I. $ZnO + C = Zn + CO$
$-86000 \quad + 29000 = -57000$

II. $2ZnO + C = 2Zn + CO_2$
$-172000 \quad 97000 = -75000$

III. $ZnO + CO = Zn + CO_2$
$-86000 \quad -29000 = \quad +97000 = -18000$

IV. $CO_2 + C = 2CO$
$-97000 \quad = +58000 = -39000$

(2) Reducing Material

There has always been some doubt as to whether reduction is by carbon or CO or both.It used to be held that it could not be done by CO but Boudouard (6) after a series of experiments concluded that carbon does not act directly on ZnO but is transformed to CO which causes the reduction.Zinc oxide can only be reduced by CO so long as the concentration of the CO_2 is very small.The CO would not reducing at 1000°C. until the total of CO_2 in the gas amounted to 0.1%.With a higher total of CO_2,zinc would be oxidized.At 1125°C.the CO_2 may amount to 0.2%.

Ingalls states that the mixture of ore and carbon should be intimate, the more perfect the mixture the more perfect the result. The reducing materials should be low in volatile matter,the substitute of it,coke alone does not give the desired results as it lacks certain quantities of hydrocarbons.The material should be also low in sulphur,moisture, and ash.It should not like a sponge absorb the slag that is formed during distillation.

Some of the reducing agents used in this work did not fulfil these requirements as it was desired to show by actual recovery that certain materials are not suitable as reducing substances.

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(6) O. Boudouard,Ann.Chem.et de Phys. 7,XXII. 16.

The materials used in this work were of a solid nature or mixtures of solids and crude petroleum. Coke, coke and oil, hard pitch, culm, culm and oil, charcoal, lignite, and calcium carbide were all tried in different combinations with varying results. 40% culm was taken as the standard for comparison as it is approximately this amount that is used in actual practice.

(5) Operation.

After the retort had been put in position, the gas was turned on and the furnace slowly heated up until the retort was a cherry red inside. The charge, which had been made up and mixed previously, was poured into a scoop with a long handle. The scoop, carrying the portion of charge was inserted into the furnace as far as it would go and then turned over, thus depositing the charge. Another rod carrying a disc that was somewhat smaller than the inner diameter of the retort was used to push the charge toward the rear. By this means the retort was filled to within a few inches of the entrance and to a height of a quarter of an inch from the top. After the entire charge was placed, a thin rod was pushed thru the length of the charge to make a passage for the gases formed.

At first, a condenser made of the same material as the retort was used but this proved unsuccessful because of its intense absorption of the condensed zinc. Then a quartz tube of [illegible] in. diameter was tried in various positions and the best place was found to be one where the condenser projected two inches inside the retort. It was hard to keep the condenser hot enough but after opening a crack in the front wall of the furnace, a flame poured out in sufficient volume to keep the rear of the condenser hot. The space between the top of the condenser and the inside roof of the retort was plugged up with wet fire clay. This caused considerable trouble

When it was time to remove the condenser from the charge or the clay luted on during distillation. We first turned up [illegible] the zinc. With all openings plugged up and the mouth of the condenser plugged with some loose culm, the gas and air were gradually increased to full force. The hydro-carbons started to come off immediately and for a short time were hot enough to burn with a long flame. After a half to three quarters of an hour the flame changed to a shorter one and the color changed from yellow to the blue of burning CO intermingled with the green of zinc and the yellow of sodium.

The first draw was made after two hours by removing as much of the culm as possible and discarding it. In actual practice the whole plug is kept along with the blue powder but in our case the plug is far greater in proportion to the blue powder than that in practice where larger quantities of blue powder are obtained. The remaining culm was broken thru with a rod having a small disc fastened to its end. The molten zinc was pulled out and all the blue powder that had formed. This is separated by a 20 mesh sieve and each part weighed separately. Draws were made each hour after that and the metal and blue powder weighed. The end of the distillation was reached when the flame died down although there was still considerable heat present. It takes a little experience to tell whether the flame has died down from lack of heat or else that all the zinc has distilled off. After the last draw has been made, the furnace is allowed to cool down; the condenser is removed, and the residue remaining in the retort is withdrawn. They are later weighed, a representative sample taken which is later analyzed for zinc. The same thing is done with the blue powder.

It took about four runs before the retort had soaked up enough zinc to make an inner lining of slag that would prevent further soaking and give constant results in the condenser, To help the slagging or glazing process, about 20 grams of salt were added to each charge.

The greatest difficulty met with during the operations was that the fire had to be turned low over night for safety, and this subsequent cooling after heating to 1150°C. is more than any retort can stand. It usually happened that after four trial runs had been made, the retort would develop cracks and have to be replaced. The last retort used ran for twelve operations and was still in good outside condition. The inside was so glazed and had so many bubbles of slag formed on its walls that to be emptied it had to be removed from the furnace and inverted. According to all laws governing retorts, they should all have broken after the first run and two operators of zinc smelters expressed wonder that they stood up as long as they did. It was undoubtedly due to the excessive glaze and the small size that they kept together at all.

Following is a description of the materials used for the charges.

The ore was roasted zinc blende in use at the United Zinc Smelting Corp. and had the following analysis: Zn 67.46% Fe.2.55% Pb. 1.04%.

The coke was taken from the pile at the above plant.

The oil used was crude petroleum.

The charcoal was powdered birch charcoal.

The lignite was powdered S.Dakota lignite.

The pitch was obtained from the Fuel Laboratory of the University of Illinois.

The CaC_2 was commercial carbide.

The coke was low temperature coke produced in the Fuel Laboratory of the University of Illinois.

PLATE No. I.

Photos Showing Furnace In Operation, Along With Retort Mold, Retort, Pyrometer, and Charging Tools .

PLATE II.

DETAILS OF FURNACE

Scale. 1½ IN. = 1 FT.

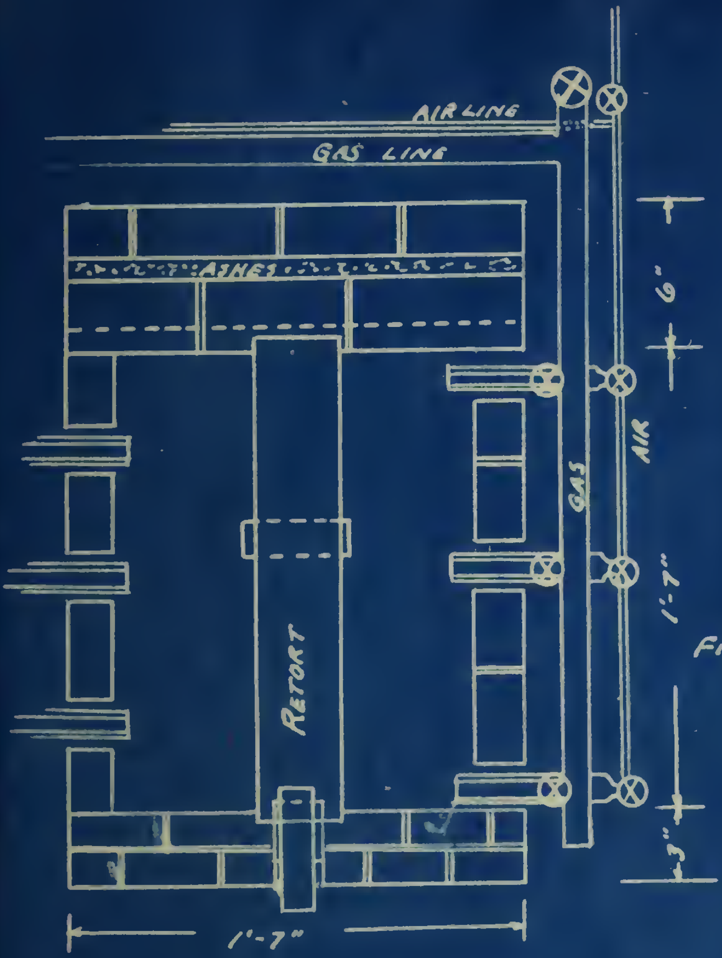

FIG. B.

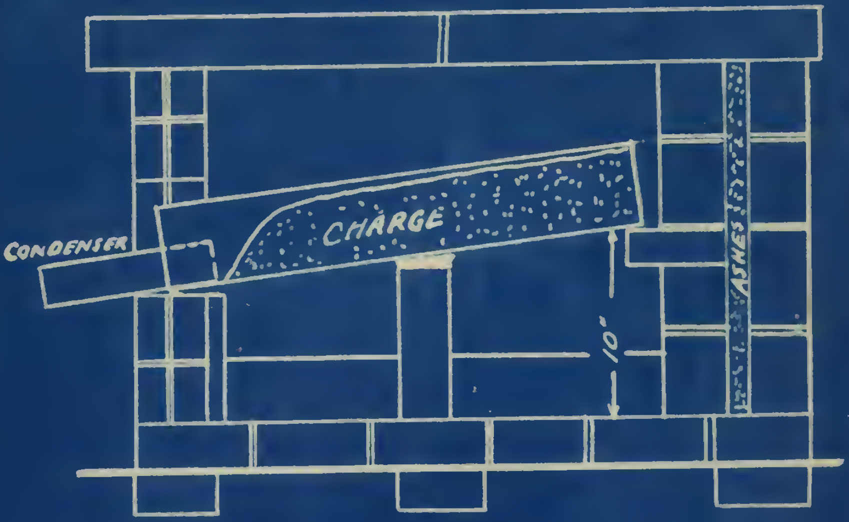

FIG. A.

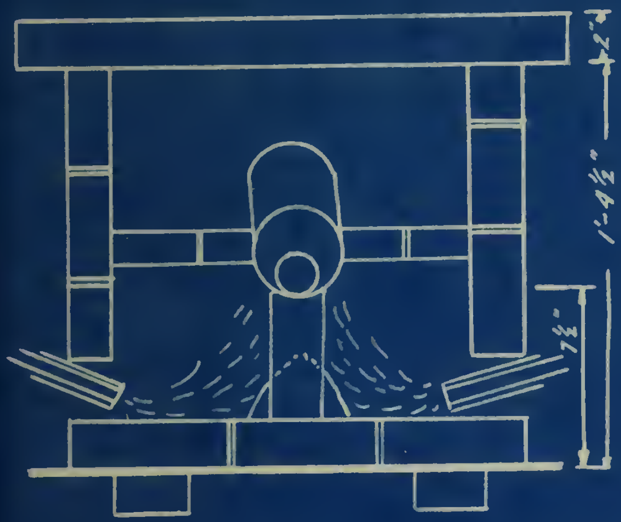

FIG C.

TABLE No.2

Showing how the absorption of zinc in the retort affects the recovery.

Times Used:	Charge	Wt. Metal Recovered	Wt. Blue Pdr.	Time for Distillation.
2nd.	same	84 grams	38 grams	52 min.
3rd.	same	103.7 "	75.6 "	[illegible] "
4th.	same	[illegible].2 "	38.2 "	34 "

TABLE No.3

Showing that the time required or that the rapidity of distillation does not affect the recovery if the distillation is carried to completion.

Charge	1st. Frac. Metal	Bl.Pd.	2nd. Frac. Metal	Bl.Pd.	3rd. Frac. Metal	Bl.Pd.	Total Metal	Bl.P.	Time
Same	65.0	14.0	66.0	7.2	33.6	1.7	165.4	22.9	44
"	130.5	15.[illegible]	35.[illegible]	3.0	5.5	2.8	171.0	26.	52

TABLE No.4

Showing the percent recovery in metal, blue powder and total recovery that was obtained from each charge.

Charge No.	Wt ore charged in grams.	Reducing agent in grams.	% of the charge	Percent Recovery Metal	Bl.P.	Total
1	500	Coke [illegible] Oil [illegible]	30 20	[illegible]	[illegible]	[illegible]
3	500	Pitch [illegible]	[illegible]	[illegible]	[illegible].5	[illegible]
[illegible]	500	Coke [illegible]	[illegible]	50.[illegible]	[illegible].6	[illegible]
4	500	Pitch 300	60	[illegible]	10.[illegible]	[illegible]
5	500	Culm 200	40	56.3	[illegible]	[illegible].2
6	500	Culm 250	50	[illegible]	2.[illegible]	[illegible]
7	500	Culm 200 Oil 50	40 10	[illegible].5	[illegible]	[illegible].1
8	500	Culm 150 Oil 100	30 20	23.6	1.4	25.0
9	400	Charcoal 200	40	70.0	1.2	71.2
10	500	Lignite 250	50	62.3	2.4	64.7
11	400	CaC2 340	85	23.9	1.1	25.0

TABLE No.5

Showing the different effects on the residues by the different charges.

A.

Charge No.	Wt. Residues
11	400 grams
8	400 "
7	255 "
4	250 "
1	235 "
6	205 "
10 and 3	190 "
5	180 "
9	160 "
2	154 "

B.

Charge No.	% Zn. in Residues
8	45.18
10	41.20
9	25.74
7	24.47
3	12.27
2	11.97
*5	11.27
1	9.50
4	9.20
6	9.18
11	—

C.

Charge No.	% of Charged Zn. in Residues.
8	58.10
10	25.2
9	15.8
7	10.9
4	6.9
1	6.5
3	6.5
5*	6.5
6	5.5
2	5.4

D.

Charge No.	% of Zn. lost thru Volatilization etc.
3	45.10
4	45.4
2	33.5
*5	33.5
7	22.4
1	22.1
8	17.0
10	12.1
9	7.0
6	5.8

PLATE No III.

COMPILED DATA SHEET

	CHARGED		RECOVERY							RESIDUES				UNRECOVERABLE LOSSES	
CHARGE No	TIME IN HOURS	UNITS OF ZINC GRAMS	METAL IN GRAMS	BLUE POWDER IN GRAMS	% ZINC IN BLUE POWDER	UNITS OF ZINC IN BLUE POWDER	TOTAL UNITS GRAMS	% RECOVERY	% INCREASE OVER CHARGE No 5	WT. IN GRAMS	% ZINC	UNITS OF ZINC GRAMS	% OF CHARGED ZINC	UNITS OF ZINC GRAMS	% OR CHARGED ZINC
1	3¾	337	228.2	38.2	41.66	15.9	244.1	72.4	+14.2	233	9.38	21.8	6.5	71.1	21.1
2	4¼	337	170.2	34.	45.83	15.6	185.8	55.1	-3.1	154	11.97	18.4	5.4	132.8	39.5
3	5¼	337	131.	26.5	70.89	18.8	149.8	44.4	-13.8	180	12.27	22.1	6.5	165.1	49.1
4	5½	337	97.3	84.6	75.21	63.6	160.9	47.7	-10.5	250	9.28	23.2	6.9	152.9	45.4
5	4⅙	337	190.	14.5	43.45	6.3	196.3	58.2		190	11.27	21.4	6.3	119.3	35.5
6	5½	337	286.	24.6	40.03	9.8	295.8	87.7	+29.5	203	9.18	18.6	5.5	22.6	6.8
7	4	337	220.	14.0	35.28	4.9	224.9	66.7	+8.5	255	14.47	36.9	10.9	75.6	22.4
8	4	337	80.	15.0	=	=	=	25.?	-35.2	400	49.18	196.7	58.1	=	17.?
9	4	270	189.0	39.5	49.22	19.4	208.4	77.2	+19.0	166	25.74	42.7	15.8	46.8	7.0
10	5	337	210.	24.	33.89	8.1	218.1	64.7	+6.5	190	41.20	78.3	23.2	40.6	12.1
11	4	270	64.	9.0	=	=	=	25.?	-35.2	480	=	=	=	=	?

PLATE Nº IV

CHART SHOWING COMPARATIVE RECOVERIES

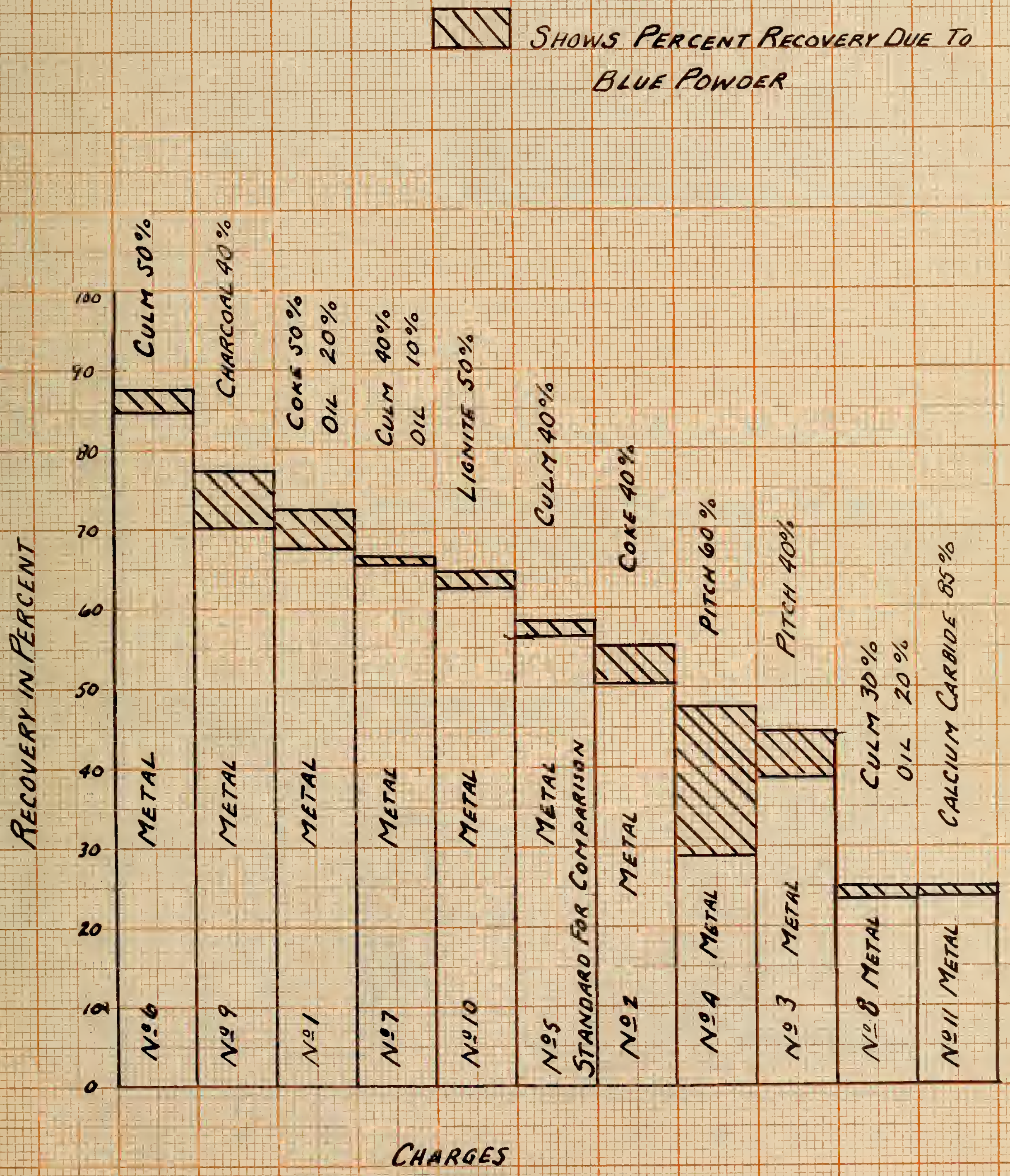

PLATE Nº V.

CHART SHOWING PERCENT OF CHARGED ZINC LOST THRU VOLATILATION AND ABSORBTION, THUS: ▨

PERCENT OF CHARGED ZINC LEFT IN RESIDUES, THUS: ☐

V.

CONCLUSION

While only a beginning was made in the search for other reducing agents,yet the results were very gratifying in that they showed many latent possibilities of development.With the coming use of poorer grades of coals,it is important that their capacities in the zinc industry be fully understood for it will not always be possible to use anthracite culm.In after years,when lignites have become usable,it may be possible to use these fuels in the part of the country where they are produced.Since the making of coke is the most economical way in which to use coal and thus obtain its by-products ,the ability of the zinc industry to use this agent would be a help in the much needed conservation of our coal supplies.The development of low temperature coke will give a coke containing some volatile matter in sufficient quantity to make it answer the requirements of a good reducing agent.

This research in reducing agents needs far greater attention than it receives, the smelters being loath to try anything different than that which is in present use.